Interpenetrated polymer networks based on commercial silicone elastomers and ionic networks with high dielectric permittivityand self-healing properties

Ogliani, Elisa; Yu, Liyun; Skov, Anne Ladegaard

Publication date:
2016

Document Version
Peer reviewed version

EuroEAP 2016
International conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles
Helsingør (Copenhagen), Denmark, 14-15 June

DTU Danmarks Tekniske Universitet

Poster ID: 2.2.5

Interpenetrated polymer networks based on commercial silicone elastomers and ionic networks with high dielectric permittivity and self-healing properties

Elisa Ogliani (1), Liyun Yu (1), Anne Ladegaard Skov (1)

Contact e-mail: al@kt.dtu.dk

The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Abstract

Recently, interpenetrating polymer networks (IPNs) based on covalently cross-linked commercial silicone elastomers and ionic networks from amino- and carboxylic acid- functional silicones have been designed, in order to obtain dielectric elastomers (DEs) with very high dielectric permittivity and to reduce the driving voltage required for the actuation process. These novel systems provide both the mechanical stability and the high breakdown strength given by the silicone part of the IPNs and the high permittivity and softening effect of the ionic network. A further advantage shown by the IPNs is the self-healing properties, which is a promising result in order to increase the life-time of the DEs.

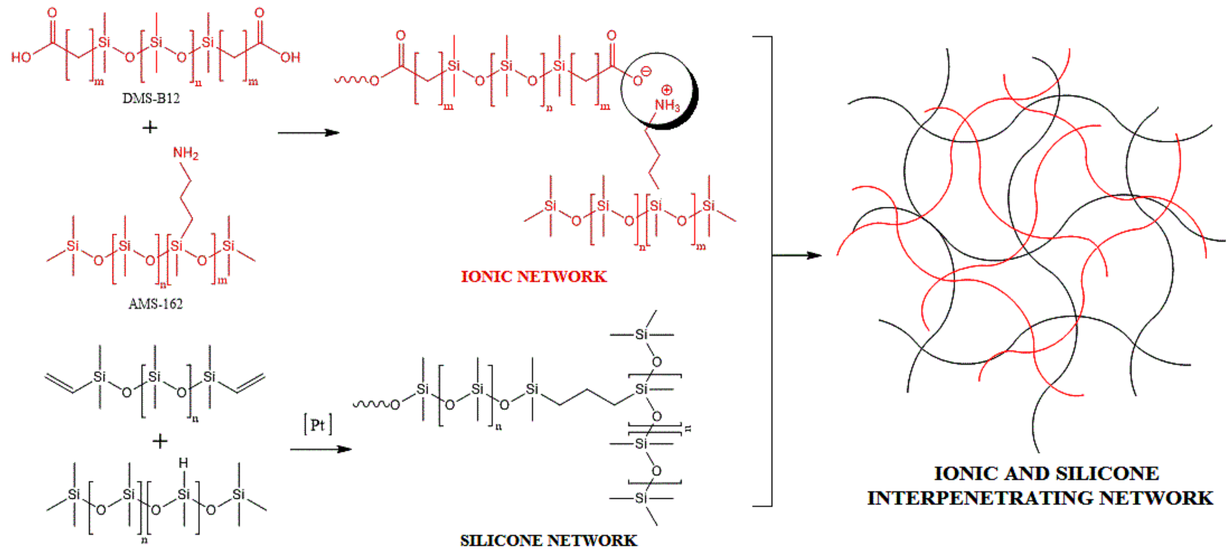


Figure 1 – Reaction scheme for the preparation of the interpenetrating polymer networks (IPNs).

Ionic networks were prepared mixing stoichiometric amounts of carboxydecyl-terminated PDMS (DMS-B12) with amino-functional PDMS (AMS-162). Once the protonation of the amino groups and the formation of the ionic bonds were obtained, the networks were mixed with various commercial silicone elastomers matrices in different ratios (Figure 1). Silica particles were also added in order to reinforce the samples. The goal was to elucidate the effect of the different formulations on the properties of the final systems.

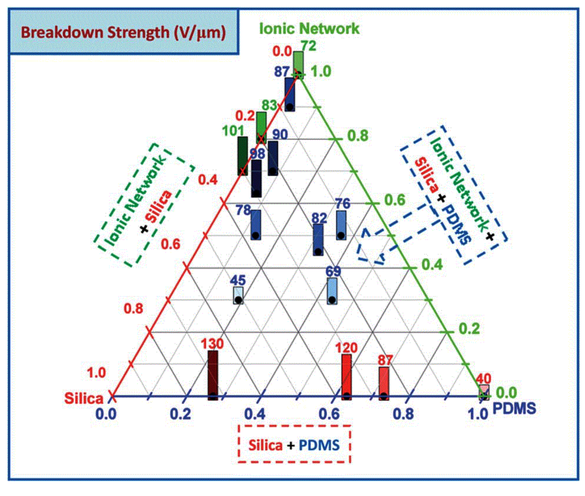
Viscoelastic properties

According to the expected **softening effect**, the pure ionic network had a lower Young modulus than the commercial elastomers. Upon addition of silica particles, both the Young modulus and the viscous loss increased, since the silica particles provides strong interactions. The mechanically best IPNs (Table 1) were achieved with the commercial elastomer LR3043/30: these systems showed a decrease in the Young modulus proportional to the increased amount of ionic network concentration, without viscous losses tan $\delta_{(rheo)}$ being affected. In addition, tan $\delta_{(rheo)}$ did not increase upon addition of silica particles.

Table 1 – Summary of Young modulus (Y) and the viscous losses tan $\delta_{(rheo)}$ at 0,01 Hz.

		Y= 3G' [kPa] (0,01 Hz)	Tan $\delta_{(rheo)}$ (0,01 Hz)
Pure PDMS		64,3	0,06
Commercial silicone LR3043/30		252,3	0,08
AMS162 + B12		37,3	0,01
IPNs LR3043/30 : (AMS162+B12)	**70 wt% : 30 wt%**	255,1	0,10
	50 wt% : 50 wt%	113,7	0,08
	30 wt% : 70 wt%	30,9	0,05
	10 wt% : 90 wt%	30,5	0,03

Dielectric breakdown strength



The **high breakdown strengths** observed are provided by the silicone part of the IPNs. The BD strengths of the IPNs were proved to be higher than the reference PDMS, ranging from 45 V/µm to 90 V/µm. These results enhance the performance of the IPNs, since the suppression of the driving voltage for the actuation process is desired.

Figure 2 – Dielectric breakdown strengths as a function of composition.

Dielectric properties

The **dielectric permittivity of the IPNs is very high** at low frequencies (0,1 Hz, Figure 3) and ranges from $\varepsilon' = 6,7$ to 2×10^3: in addition, the increasing of ε' is in line with the increasing of the ionic network concentrations in the prepared samples.

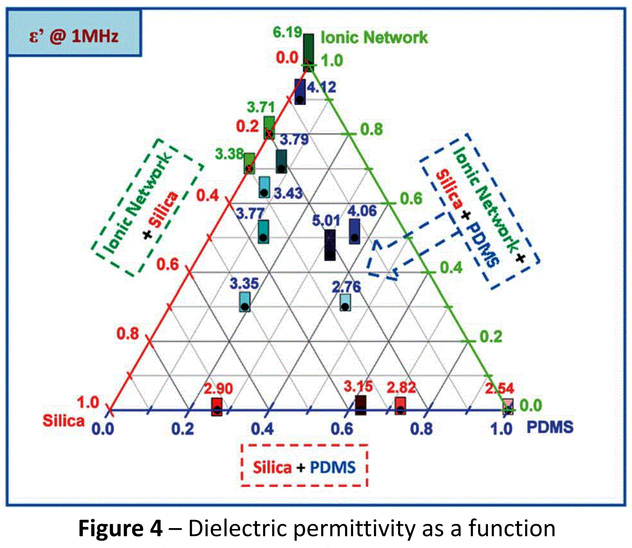


Figure 4 – Dielectric permittivity as a function of composition of IPNs at 1 MHz.

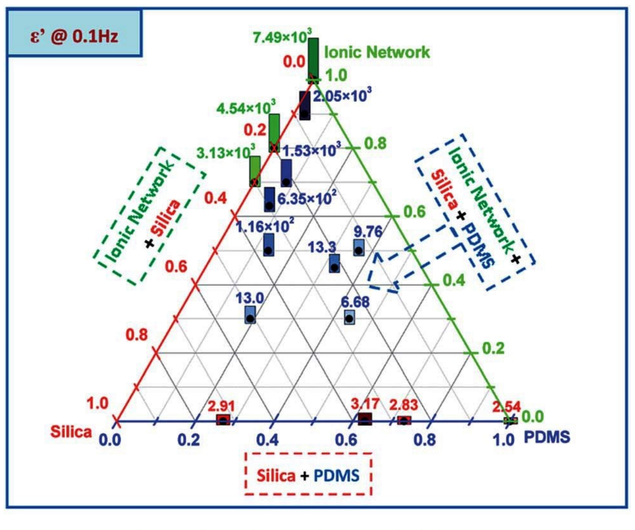


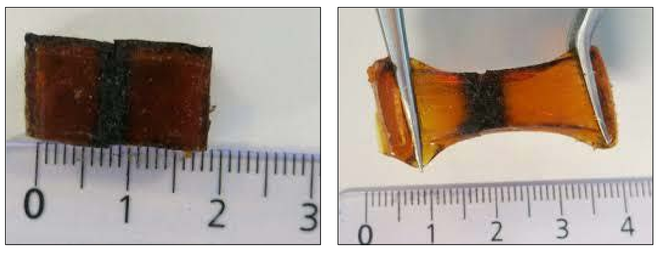
Figure 3 – Dielectric permittivity as a function of composition of IPNs at 0,1 Hz.

At higher frequencies (Figure 4) the highest ε' corresponds to the sample with 50% ionic network and 50% silicone network. Furthermore, at 1 MHz a proportional increase of ε' with higher ionic network concentration was not observed.

Self-healing properties

An additional and promising advantage achieved by the IPNs is represented by the self-healing properties. The ionic part of the interpenetrating networks, based on non-covalent interactions, makes the systems capable of recovering both upon mechanical rupture and upon electrical breakdown: Figure 5 shows how they support **more than 100% elongation of the reassembled samples**.

Figure 5 – Self-healing properties of the reassembled IPN sample (dark areas are from the cutting line).



Pure ionic network

In order to investigate further the properties of the pure ionic network and the development of the reaction of the ionic bond formation, samples composed of different ratios (r) of DMS-B12/AMS-162 were tested. In particular, after the curing of the samples (r=0,5; r=1; r=1,5), the trend of the viscoelastic and dielectric properties with time was checked. As shown in Figure 6, both the permittivity ε' and the storage modulus G' decrease over time.

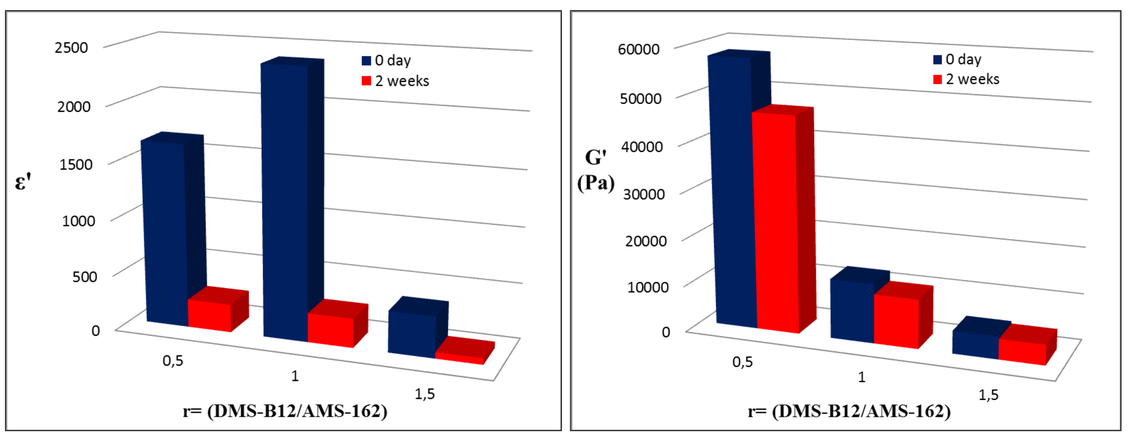
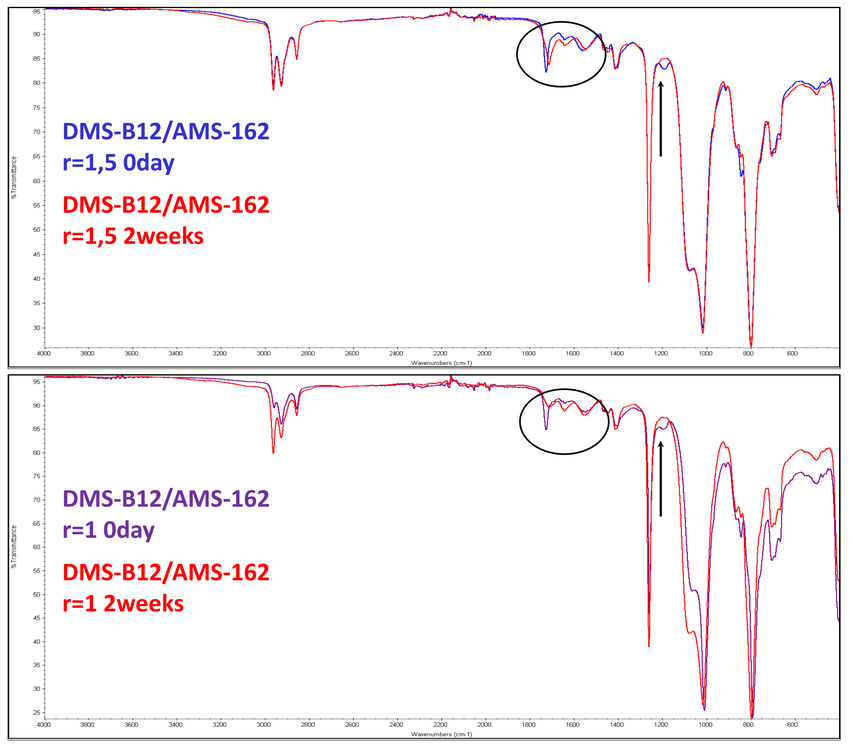


Figure 6 – Trend of dielectric permittivity ε' and storage modulus with time of the pure ionic networks at low frequencies.

In addition, the IR of the pure ionic network samples before the curing was checked at room temperature in order to analyze the stability of the systems and verify changes in the spectra with time. The sample (DMS-B12/AMS-162)=0,5 was proved to be the most stable; in the spectra corresponding to the sample r=1 and r=1,5 (Figure 7) it is possible to observe the shift of the carbonyl stretch from 1750 cm^{-1} (corresponding to the carboxylic group) to 1580 cm^{-1} (associated to the carboxylate). In addition, the peak at ~1180 cm^{-1} from the pure DMS-B12 disappeared.

Figure 7 – FT-IR spectra of the pure ionic samples (DMS-B12/AMS-162)=1,5 and (DMS-B12/AMS-162)=1.



References

[1] L. Yu, F. B. Madsen, S. Hvilsted, A. L. Skov, "Dielectric elastomers, with very high dielectric permittivity, based on silicone and ionic interpenetrating networks", *RSC Adv.* **2015**, 5, 49739.
[2] L. Yu, F. B. Madsen, S. Hvilsted, A. L. Skov, "High energy density interpenetrating networks from ionic networks and silicone", *Proc. SPIE* **2015**, 9056, 90560C-1.